

First-Principles Calculation of Mg(0001) Thin Films: Quantum Size Effect and Adsorption of Atomic Hydrogen

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We have carried out first-principles calculation of Mg(0001) free-standing thin films to study the oscillatory quantum size effect exhibited in the surface energy, work function, interlayer relaxation, and adsorption energy of the atomic hydrogen adsorbate. The quantum well states have been shown. The calculated energetics and interlayer relaxation of clean and H-adsorbed Mg films are clearly featured by quantum oscillations as a function of the thickness of the film, with oscillation period of about 8 monolayers, consistent with recent experiments. The calculated quantum size effect in H adsorption can be verified by observing the dependence of H coverage on the thickness of Mg(0001) thin films grown on Si(111) or W(110) substrate which has been experimentally accessible.

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I. INTRODUCTION

When the thickness of thin metal films approaches the nanoscale, the oscillatory quantum size effects (QSE) associated with electronic confinement and interference will occur^{1,2,3,4} due to the splitting of the energy-level spectrum into subbands normal to the plane of the films. Confinement of electrons often leads to strongly modified physical properties. It has been shown that a change in film thickness by just one atomic layer can result in property variations on the order of $1/N$, where N is the thickness of the film in terms of monolayers (ML). The oscillatory QSE have long been clearly observed in ultrathin metal overlayers on metal substrates⁵, mostly involving noble metals. On the other hand, thin metal films on semiconductors may be the basis for novel devices utilizing quantum-well states (QWS). Thus recent systematic experimental and theoretical investigation of the QSE has mainly been focused to Pb films deposited on Si(111)^{6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21} substrate.

In this paper we present a detailed first-principles study of the electronic structure and adsorption energetics of Mg(0001) free standing films. The QSE in some other free-standing metal films such as Al^{22,23,24}, Li²⁵, and Pb^{26,27} have been theoretically reported in previous references. The present study is directly motivated by the recent experimental demonstration that highly perfect ultrathin epitaxial Mg(0001) films can be grown on Si(111) substrate by low-temperature deposition and annealing²⁸, and on W(110) substrate^{29,30,31}. Using angle-resolved photoemission spectroscopy (ARPES) technique, Aballe *et al.*²⁸ have showed that each time a QWS state falls in the wave-vector and energy range of the upper branch of the Mg *sp* band, a new peak is visible in the photoemission spectrum, with the thickness interval between the two sequential peaks being about 8 ML. Schiller *et al.*²⁹ have extensively measured the electronic structure of magnesium from Mg(0001) monolayers to bulk. More recently, Koitzsch *et al.* and Schiller *et al.* have reported the spin-splitting effects in ultrathin Mg(0001) films due to the coupling of the

Mg(0001)/W(110) interface electronic structure and the QWS states. It is expected that further work related with the Mg(0001) thin films will be reported afterwards. From this aspect a thorough theoretical investigation of the QSE in Mg(0001), including the energetics and the interlayer relaxation, is necessary and will be helpful for the future experimental reference. It should be mentioned that the theoretical study of QSE on Mg(0001) was initiated by Feibelman²².

The other object in this paper is to study the QSE character in the atomic adsorption energetics, which has been neglected by most of the previous studies. Since the adsorption property is closely characterized by the chemical bonding between the adsorbate and the surface of the substrate, thus when the substrate is ultra-thin, the QSE in the substrate will also influence the behavior of the surface adsorption. Here as a case study we choose the atomic hydrogen as the adsorbate on Mg(0001), since H is the most simple element, also since the influence of atomic hydrogen adsorption on the surface electronic structure of the metals has been extensively studied without emphasis on QSE. Our results show that in the ultrathin Mg(0001) films, the adsorption energy of atomic H displays a well-defined QSE.

This paper is organized as follows: In Sec. II, the *ab initio* based method and computational details is outlined. In Sec. III, the surface properties of the Mg(0001) films, including the electronic structure, surface energy, work function, and interlayer relaxation, as a function of the thickness of the films, are presented and discussed. Also the properties of adsorption of atomic hydrogen monolayer onto Mg(0001) surface is discussed in detail by presenting the sensitivity of the adsorption energy to the thickness of the Mg(0001) films. Finally, Sec. IV contains a summary of the work and our conclusion.

II. COMPUTATIONAL METHOD

The calculations were carried out using the Vienna *ab initio* simulation package³² based on density-

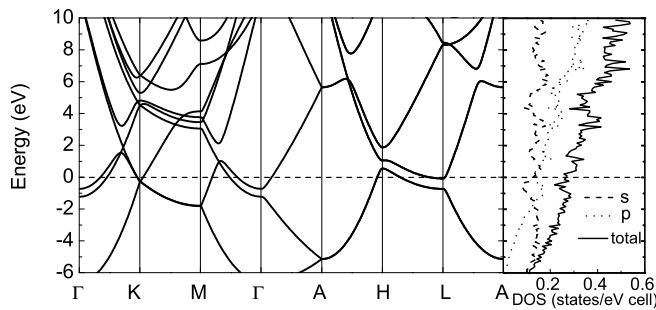


FIG. 1: GGA energy bands and density of electron states (right panel) of hcp bulk Mg. The dashed line denotes Fermi level.

functional theory with ultrasoft pseudopotentials³³ and plane waves. In the present film calculations, free-standing Mg(0001) films in periodic slab geometries were employed. The periodic slabs are separated by a vacuum region equal to 20 Å. In all the calculations below, a surface (1 × 1) was employed for the supercell slab. The Brillouin-zone integration was performed using Monkhorse-Pack scheme³⁴ with a 11 × 11 × 1 k -point grid, and the plane-wave energy cutoff was set 250 eV. Furthermore, the generalized gradient approximation (GGA) with PW-91 exchange-correlation potential has been employed with all atomic configurations fully relaxed. First the total energy of the bulk hcp Mg was calculated to obtain the bulk lattice constants. The calculated a - and c -lattice parameters are 3.201 Å and 5.186 Å, comparable with experimental³⁵ values of 3.21 Å and 5.213 Å, respectively. The use of larger k -point meshes did not alter these values significantly. A Fermi broadening of 0.1 eV was chosen to smear the occupation of the bands around E_F by the Fermi-Dirac function.

III. RESULTS AND DISCUSSION

Band structure.— We first studied the properties of electronic structures of Mg(0001) films. As a first step, we present in Fig. 1 the band structure and the density of states (DOS) of bulk hcp Mg. One can see that the DOS of bulk Mg is nearly free-electron like ($\simeq \sqrt{\epsilon}$). This is different from its close neighbor Be whose DOS resembles somewhat that of a semiconductor due to the absence of core electrons in Be atoms. Also one can see from Fig. 1 that there are two filled states at Γ with energies around 1 eV, while in the case of Be the corresponding states are above the Fermi energy. Although the outmost electronic configuration of elemental Mg is $3s^2$, one can see from Fig. 1 that the p -orbital component in bulk Mg plays as well an important role around E_F .

The electronic structure properties of Mg(0001) film are shown in Fig. 2 as a function of the thickness of the film. Here we only plot the energy levels at Γ point without interlayer relaxation. The energy zero is set at

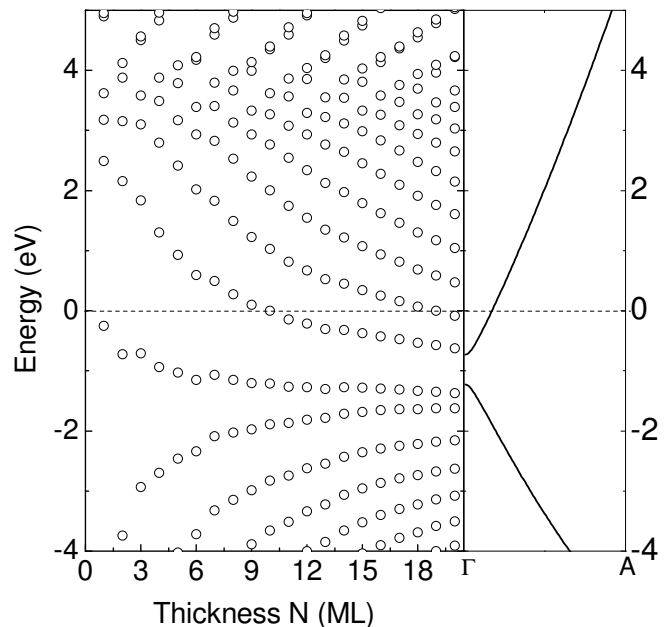


FIG. 2: Calculated (GGA) energies at Γ in Mg(0001) thin films as a function of thickness, with the energy set to zero at the Fermi level. The right panel replots the bulk energy dispersion in the [0001] direction.

the Fermi level of each film. Interlayer relaxation effect has also been studied and it is found that the overall thickness dependence of the energies is similar to that without relaxation. For comparison and illustration, the bulk energy dispersion along the [0001] ($\Gamma \rightarrow A$) direction [see Fig. 1], which determines the energy range for the quantum well states, is plotted again in Fig. 2 (right panel). One can see that the energy gap at Γ is small due to the hybridization of Mg s and p orbitals, with the energy of ~ 0.5 eV. The QWS states arise from the upper band. When the thickness of the film is increased to ~ 8 ML, then a QWS state, with the energy crossing the Fermi level, occurs. The next energy crossing with the Fermi level occurs at the film thickness of 16 ML. Our calculated results of QWS states are in good agreement with recent experimental ARPES measurement.

For sp metals the QWS states are often analyzed in the framework of the phase accumulation model^{36,37}. Here the free-standing Mg(0001) film is considered as a quantum well confining electrons between the two vacuums in the slab. Only such k_{\perp} (perpendicular component of bulk wave vector) values of the electrons are allowed that fulfill the stationary state condition for integer n ,

$$2k_{\perp}Nd + 2\Phi = 2\pi n, \quad (1)$$

where N is the number of atomic layers in the film, $d = c/2$ the interlayer spacing, and Φ the phase shift of the electronic wave function upon reflection at the film-vacuum interface. Using Eq.(1) one can calculate the periodicity for the QWS states crossing the Fermi

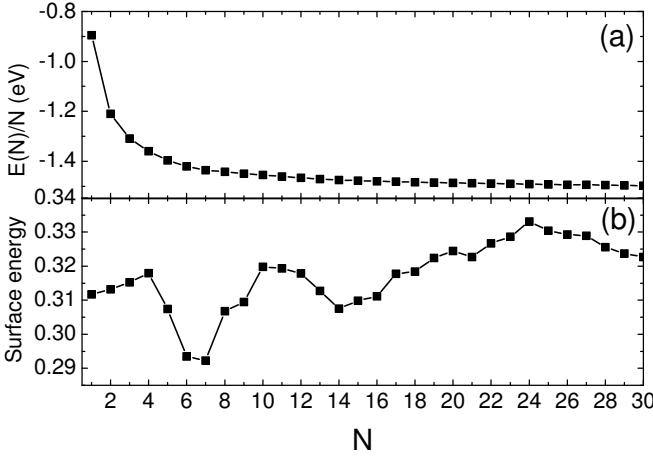


FIG. 3: (a) Monolayer energy $E(N)/N$, (b) corresponding energy difference $\Delta E(N)$, and (c) surface energy for fully relaxed Mg(0001) 1×1 slabs as a function of thickness.

level, $\Delta N = \pi/(k_{\perp}^f d)$, where k_{\perp}^f is the perpendicular component of Fermi wave vector. From the right panel in Fig. 2, one can see that the upper branch of the bulk sp band runs through about 25% of the Brillouin zone, $k_{\perp}^f = 0.25\pi/c$. One gets $\Delta N = 8$. Therefore a new QWS state occurs every 8 ML, which is verified in the left panel in Fig. 2 that an energy branch moves down, crossing the Fermi level for every incremental increase in the film thickness of 8 ML.

Energetics.— Figure 3(a) shows the total energy $E_t(N)/N$ per ML as a function of the thickness of the Mg(0001) film. The atoms in the slabs have been fully relaxed during calculations. One can see from Fig. 3(a) that with increasing the thickness, $E_t(N)/N$ gradually approaches a constant value which in the limit is equal to the energy per atom in the bulk Mg.

An energetic quantity more suitably tailored to the QSE is the surface energy which is defined as one-half of the energy difference between the film and the bulk with the same number of atoms, including the proper subtraction of a term linear in N ³⁸. The thickness dependence of surface energy is shown in Fig. 3(b). It reveals that consistent with the result of the electronic structure in Fig. 2, the surface energy follows a simple oscillatory form with the period of $\Delta N \simeq 8$. These oscillations arise from the occupation of electronic levels close to Fermi surface. Also one can see that the oscillation pattern is not as good as one expects. This is due to the fact that the atomic arrangement in the slabs has been fully relaxed during the calculation.

Figure 4 (line with triangles) shows the work function as a function of the thickness of Mg(0001) film for relaxed atomic geometry. One can see the work function is also featured by an oscillatory form multiplied by a damping factor. The oscillation period in thickness is again $\Delta N \simeq 8$.

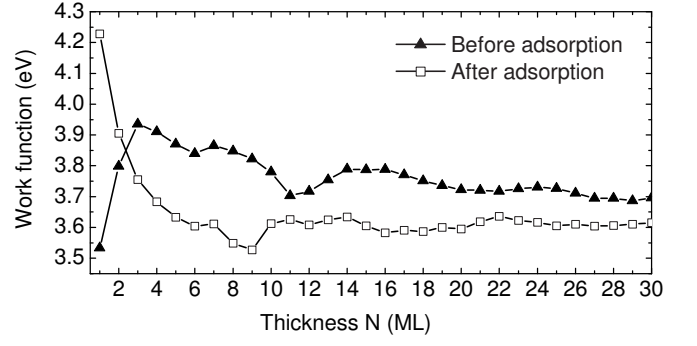


FIG. 4: Work function of clean and H-adsorbed Mg(0001) thin films as a function of thickness.

TABLE I: Interlayer relaxations given in percent, $\Delta d_{i,i+1}$, of Mg(0001) as a function of the thickness of the film.

N	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	Δd_{56}	Δd_{67}
2	+8.387					
3	+6.985	+6.995				
4	+1.766	-2.104	+1.779			
5	+1.593	-0.672	-0.67	+1.595		
6	+0.785	-1.161	+0.604	-1.169	+0.798	
7	+2.787	-0.282	-0.051	-0.1	-0.237	+2.817
8	+2.323	-0.741	-0.605	-0.1	-0.652	-0.7
9	+1.603	-0.903	-0.192	-0.46	-0.46	-0.187
10	+1.438	-1.075	-0.053	-0.341	-0.452	-0.342
11	+0.654	-1.1	+0.066	-0.213	-0.34	-0.34
12	+0.537	-1.089	+0.212	-0.583	+0.059	-0.533
13	+0.898	-1.304	0.227	-0.358	-0.375	-0.105
14	+1.172	-1.197	0.115	-0.412	-0.236	-0.391
15	+1.723	-0.93	-0.264	-0.194	-0.468	-0.208

Interlayer relaxation.— The interlayer relaxation, $\Delta d_{i,i+1}$, is given in percent with respect to the unrelaxed interlayer spacing, d_0 , i.e., $\Delta d_{i,i+1} = 100(d_{i,i+1} - d_0)/d_0$. $d_{i,i+1}$ is the interlayer distance between two adjacent layers parallel to the surface calculated by total energy minimization. $d_0 = c/2$ is the bulk interlayer distance. As mentioned above, all layers in the slab were allowed to relax. Obviously, the signs + and - of $\Delta d_{i,i+1}$ indicate expansion and contraction of the interlayer spacings, respectively. The relaxation of Mg(0001) surface as a function of the thickness of the film is summarized in Table I. Furthermore, the interlayer relaxations are also plotted in Fig. 5 for more clear illustration. One can see: (i) The two outmost layers relax significantly from the bulk value, in agreement with experimental observation⁴⁰. In the whole range of layers that we considered, the topmost interlayer relaxation is always outward ($\Delta d_{1,2} > 0$). The value of $\Delta d_{1,2}$ starts from +8% for a slab with only 2 ML, and approaches a final value of $\sim 1\%$ with increasing the thickness of Mg(0001) film. In contrast to the behav-

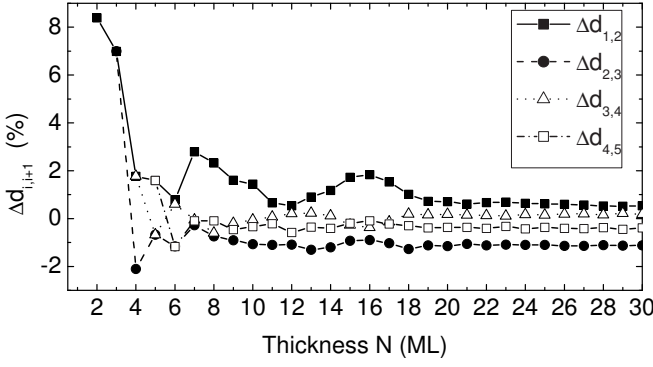


FIG. 5: Interlayer relaxations of Mg(0001) thin films as a function of thickness.

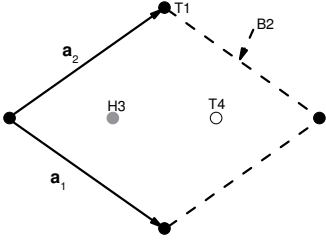


FIG. 6: The four different adsorption sites for H adatom on Mg(0001) surface.

ior of $\Delta d_{1,2}$, the second interlayer relaxation is always inward ($\Delta d_{2,3} < 0$). Note that the first interlayer separation on most metal surfaces is contracted, Mg(0001) is one of the few exceptions; (ii) The interlayer spacings oscillate as a function of the thickness of the film with a damped magnitude. The oscillation period is about 8 ML in the thickness, thus clearly indicating the QSE in the interlayer relaxation. After 30 ML, which is the maximal layers considered here, the oscillations are invisible, which suggests that the semi-infinite surface limit is now reached.

Adsorption of atomic hydrogen: QSE of binding energy.— To further illustrate the physical properties influenced by finite size of the thin films, in this section we focus our attention to the adsorption of atomic hydrogen on Mg(0001) thin films. To the best of our knowledge, the reflection of QSE by the adsorption features has been neglected by most of the previous studies.

Before we study the hydrogen adsorption properties as a function of the thickness of the film, we need to determine the energetically favorable adsorption site. Since the preference of adsorption site is not sensitive to the thickness of the substrate, thus to look for this preference, it is sufficient to give a study on the slabs with fixed thickness of Mg(0001) substrate, which at present is chosen to be 9 ML. We choose four most probable adsorption sites, namely, on-top (T1), bridge (B2), fcc (H3), and hcp (T4) sites, which are schematically in-

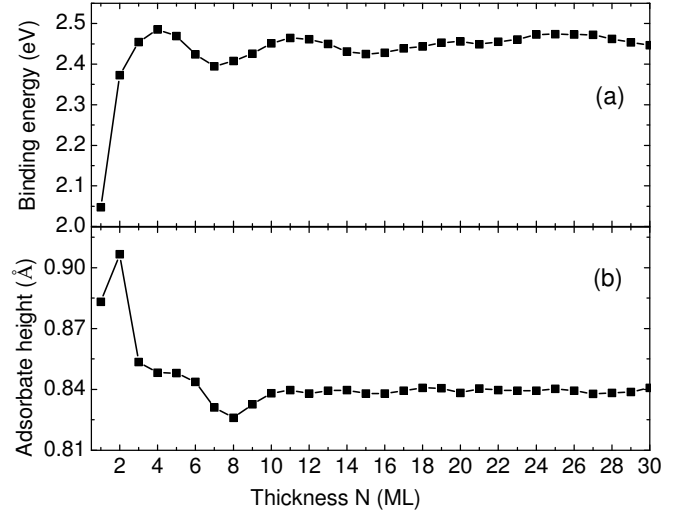


FIG. 7: Calculated (a) binding energy of H adatom and (b) adsorbate height as a function thickness of Mg(0001) films.

indicated in Fig. 6. The binding energy is calculated using the following equation: Binding energy [atomic H] = $-(E[\text{H/Mg(0001)}] - E[\text{Mg(0001)}] - 2E[\text{H}])/2$ where $E[\text{H/Mg(0001)}]$ is the total energy of a slab which consists of 9 layers of Mg atoms and one H atom on each side keeping inversion symmetry, $E[\text{Mg(0001)}]$ is total energy of the slab without H atoms, and $E[\text{H}]$ is total energy of a free H atom which is put in a supercell with the size of 10 Å. As a result, the calculated binding energy of atomic H for different adsorption configurations is 1.317 eV (T1), 2.394 eV (H3), and 2.319 eV (T4). The B2 site is unstable and after the zero-temperature relaxation, the H adatom at B2 will diffuse to H3 site. Thus the fcc (H3) site is most stable and in the following discussions, the atomic H is always put on H3 site during the simulation. Note that this H3 preference for H adsorption on Mg(0001) is different from the cases in Be(0001) and W(100) wherein the bridge-site is preferred^{41,42}.

After finding the preferred atomic H adsorption site (H3), we gave a series of calculations for the binding energy of the H adsorbate as a function of the thickness of Mg(0001) thin films. The results are summarized in Fig. 7(a). One can see that the binding energy curves up at small film thickness, followed by damped oscillations when increasing the Mg ML in the slab. Thus the binding energy of atomic H depends on the thickness of the quantum films in an oscillatory way. The oscillation period in thickness is about 8 monolayers, indicating a well-defined QSE in the adsorption of atomic H on Mg(0001). In experiment this QSE of atomic adsorption can be observed by investigating the dependence of H coverage on the monolayers of Mg(0001) thin films. Also we have calculated the H adsorbate height and the results are plotted in Fig. 7(b), which again shows the periodic oscillations indicative of QSE. Furthermore, we have calculated the work function for the H-adsorbed Mg(0001),

which is shown in Fig. 4 (line with squares). One can see that compared to the clean Mg(0001), the work function is reduced by the presence of H adlayer, implying that the charge is transferred from H to Mg. Also it shows in Fig. 4 that as in the case of clean surface, the work function of H-adsorbed Mg(0001) is oscillatory in the amplitude with respect to the thickness of the film. The oscillation period in thickness is again $\Delta N \simeq 8$.

IV. CONCLUSION

In summary, the Mg(0001) thin films have been studied by density-functional theory pseudopotential plane-wave calculations. The dependence of electronic structure, energetics, and interlayer relaxation upon the thickness of

the film has been fully investigated, clearly showing the metallic QSE of the film, in consistent with the recent experiments. We have also studied the atomic hydrogen adsorption on the Mg(0001) film. It has been shown that the adsorption energy of H oscillates with the increase of Mg monolayers in the slab. As the other energetic quantities, this oscillation in the adsorption energy can also be explained by the occurrence of the QWS states in the ultrathin metal films.

Acknowledgments

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